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A Process for Converting Corn Bran to Furfural without Mineral Acids

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Furfural is a bio-derived industrial chemical that has been identified as a platform chemical for the production of renewable fuels and chemicals. Currently, domestic feedstock and processing costs are high, so United States-based furfural production is not competative on the global market. Furthermore, furfural production costs must be much less than the current market price if it is to be competative platform for bio fuels and chemicals. An alternative low-cost feedstock for furfural is corn bran from a corn ethanol process. We have proposed a new process for producing furfural from corn bran that consumes no mineral acids. The high hemicellulose content of corn bran reduces capital and operating costs. Eliminating mineral acids reduces chemical consumption and makes the residual solids suitable for consumption as animal feed. The combination of a low cost source of hemicellulose and high valued residue could make the proposed process more economical than current processes based on corncobs.

1. Introduction

Furfural is a bio-derived industrial chemical. ¹ The reported global furfural production was 370,000 tonnes in 2016 with a market value of \$642 million and a projected market growth rate of 11% per year. ² Most furfural (60 -70%) is converted into furfuryl alcohol, which is used for foundry-sand binder resins, fiber-reinforced plastics, corrosion resistant cements, wood protection, and so forth. ^{1,3} Other uses of furfural are a solvent for extracting butadiene, and isoprene from C₄ and C₅ hydrocarbons, ⁴ a reactive solvent and wetting agent, and a control agent for parasitic worms (nematodes). ¹ The United States (US) Department of Energy (DOE) has identified furfural as one of the top 30 platform chemicals derived from biomass. ⁵

Furfural is produced exclusively from the pentose sugars in hemicellulose. In 1921, the first commercial-scale furfural process used oat hulls as the source of hemicellulose. Currently, the primary sources are corncobs and sugarcane bagasse. China is the dominant player in the furfural market, and they possess 85% of the global production capacity. Other major producers are South Africa and the Dominican Republic. No significant quantities of furfural are currently produced in the US. Since 2000, global furfural prices have been volatile. Between 2014 and 2016, price varied between \$950 and \$2200 per tonne. We surveyed recent Chinese furfural prices and

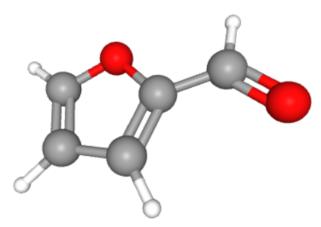


Fig. 1. Furfural molecular structure

found a range of prices from \$900/tonne to \$2300/tonne with a median of \$1350/tonne.

To be successful, a domestic US furfural plant must be profitable at world market prices. Domestic furfural production based on current process technology and corn cobs is too expensive to be competitive. US industrial consumers would like a reliable domestic source at a price of \$1200 – 1300 per tonne. To be a useful bio-derived platform chemical, the furfural price must be much lower than the current target price for industrial consumers. Based on our studies bio-derived dicyclopentadiene, the price of furfural must be less than \$1000 per tonne to be a cost-competitive platform chemical.

Biomass constitute 30% of furfural production costs, and process chemicals constitute an additional 10%. Therefore, alternative feedstocks and process technology that reduces chemical consumption are needed if US produced furfural is to be competitive in the world market and a cost-effective platform chemical. We examined alternative feedstocks and identified corn bran as promising source of furfural because of its high hemicellulose content. Also, corn bran is byproduct of ethanol product production, so furfural production based on corn bran fits well with the concept of an integrated biorefinery. In this report, we discuss a new process for producing furfural from corn bran that does not consume mineral acids.

2. Existing Processes

2.1. Hemicellulose Conversion

Furfural production involves two chemical reactions. The first reaction is acid hydrolysis to release the pentose sugars from the hemicellulose.

$$Hemicellulose + mH_2O \xrightarrow{acid} nC_5H_{10}O_5 + pC_6H_{12}O_6 + acids$$
 (1)

The second reaction is acid-catalyzed dehydration of the pentose sugars to furfural.

$$C_5 H_{10} O_5 \xrightarrow{acid} C_5 H_4 O_2 + 3H_2 O \tag{2}$$

In current commercial processes, both reactions are catalyzed by a soluble mineral acid, such as sulfuric acid. The oldest furfural process is the Quaker Oats batch process with the first commercial plant starting up in 1921. Air-dried biomass is mixed with aqueous sulfuric acid. Steam is injected to heat the slurry and to strip the furfural for the aqueous solution. Stripping of the furfural from the solution is essential to obtaining acceptable yields. Figure 3 shows a proposed mechanism for the conversion of xylose into furfural. The mechanism includes condensation reactions between furfural and the products of side reactions. When heated, furfural undergoes self-condensation reactions to produce resins. Continuous steam extraction prevents both condensation reaction with side products and resinification. Optimized versions of the Quaker Oats process are still used.

Quaker Oats developed a continuous furfural process, which they commissioned in 1966.¹ Moist bagasse was mixed with a dilute sulfuric acid solution in a horizontal auger reactor. Superheated steam is injected at multiple points along the reactor to provide heat for the dehydration reaction.¹¹ The yield for the continuous process is the same as the batch process.¹ Numerous other continuous furfural processes have been developed. Natta patented a process in which moist biomass with duillute hydrochloric acid is feed to the top of a vertical reactors.¹¹ Superheated steam is introduced at the bottom of the reactors to provide heat for the reaction and to strip the furfural from the biomass. The solid residue is removed at the bottom of the column. The ROSENLEW process is similar to the Natta process.¹¹¹²

Stripping the furfural from the liquid during the reaction increases yield by preventing side reactions. The processes described above use steam as the stripping agent, but newer processes have been proposed in which a liquid organic solvent is fed to the furfural reactor to extract the furfural from the organic phase.¹³

2.2. Purifying Furfural

Furfural and water are partially miscible. At 25°C, the solubility of furfural in water is 1.75 mole % and the solubility of water in furfural is 20.3 mole %. ¹⁴ Furfural and water form a three-phase azeotrope with

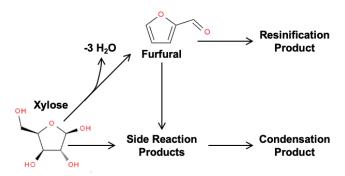


Fig. 2 Mechanism for the conversion of xylose to furfural proposed by Agirrezabal-Telleria et al.⁹

an overall composition of about 9.0 mole % furfural. Because of the partial miscibility and the resulting three-phase azeotrope, furfural and water cannot be separated by simple distillation.

The most common approach to purifying furfural is an azeotropic distillation consisting of two columns. The first column separates water from the mixture. The distillate is the azeotropic mixture that separates into two phases when condensed. The aqueous phase is used as the reflux for the first column. The organic phase is feed to a second column, which separates the furfural from the water. Like the first column, the distillate is the azeotropic mixture. The organic phase is the reflux for the second column, and the aqueous phase is recycled to the first column.

An alternative to azeotropic distillation involves a liquid-liquid extraction step. ¹⁵ Furfural is extracted from the aqueous condensate from the reactor with an immiscible organic solvent. Many possible solvents have been considered, but the most promising are benzene, toluene, and butyl chloride. Furfural does not form an azeotrope with the organic solvent, so it can be separated from the solvent with a simple distillation. The solvent extraction process is reported to be more energy efficient than the conventional azeotropic distillation. ¹⁵

3. Corn Bran

3.1. Corn Bran and Fiber Composition

According to Yadhav et al., ¹⁶ the corn fiber is obtained from the dry milling process, and it consists primarily of the fibrous pericarp of the corn kernels. Corn bran is used as low-value cattle feed, and it is rich in hemicellulose. Noureddine and Byun identified corn fiber as a potential source of furfural. ¹⁷

We reviewed published analyses of corn bran ^{18,19,20,21,22,23} and corncobs. ^{24,25} The composition of corn bran is variable, and it depends on the composition of the corn and the processing history. The reported hemicellulose content of corn bran is between 29 to 68 wt. %. The commercially available corn bran that we used in our preliminary studies contained approximately 52 wt. % hemicellulose We used a maximum likelihood analysis of the data to obtain representative compositions of corn bran and corncobs compositions. Table 1 contains the results. On the average corn bran contains on the average 12% more hemicellulose than corncobs.

3.2. Availability and Cost

The economic viability of a feedstock depends on its availability and cost. We made order-of-magnitude estimates of the potential supply of corn stover, corncobs, and corn bran base on US Department of Agriculture statistics of domestic corn production, corn ethanol production, and corn starch production. We estimated the hemicellulose content of these materials using the representative values in Table 1, and we also assumed a furfural yield of 0.42 tonne per tonne of hemicellulose. Table 2 is a summary of these estimates. The projected global furfural demand is projected to be about 550,000

Table 1. Representative compositions for corn bran and corncobs.

| Component | Composition (wt. %) | | |
|---------------|---------------------|----------|--|
| _ | Corn Bran | Corncobs | |
| Water | 7% | 15% | |
| Starch | 9% | 1% | |
| Hemicellulose | 44% | 38% | |
| Cellulose | 15% | 33% | |
| Lipids | 1% | 0% | |
| Proteins | 9% | 10% | |
| Lignin | 2% | 4% | |
| Ash | 7% | 2% | |
| Other | 5% | _ | |

2 April 2020

Table 2. Order-of-magnitude estimates of supply and potential furfural yield from corn-based biomass.

| Feedstock | Potential Supply (tonne/yr) | Hemicellulose Content (tonne/yr) | Furfural Yield (tonne/yr) |
|-------------|-----------------------------------|--|---------------------------------|
| Corn Stover | 81,000,000 | 16,000,000 | 6,800,000 |
| Corncobs | 37,000,000 | 5,900,000 | 3,100,000 |
| Corn Bran | 4,000,000 | 1,200,000 | 650,000 |

tonne/yr in 2022.² Although the potential furfural production from the other feedstocks is higher, the potential supply of corn bran is sufficient to meet the growing global furfural demand.

Currently, the primary use of corn bran is a low-grade animal feed. Based on its protein and carbohydrate, we estimated the value of corn bran as an animal feed to be \$54. ²⁶ This estimate includes transportation costs, which we estimate to be a minimum of \$27/tonne. Co-locating a furfural plant with a corn ethanol plant would eliminate shipping costs and reduce the cost of corn bran to \$27/tonne making it a very inexpensive source of furfural.

A key advantage of corn bran as a source of furfural is the value of the residue. The residue contains most of the protein, lipids, minerals, and insoluble fiber and starch of the original corn bran. We estimated that corn bran residue will contain about 20% protein and 40% neutral fiber making it more valuable per tonne as an animal feed than the original corn bran. However, to fully realize its value as animal feed, the residue must not have excessive concentrations of sulfate or other potentially harmful chemical residue.

4. Furfural Process Summary

To realize the economic advantages of corn bran, we developed a furfural process that does not use mineral acid as a catalyst. We expect the furfural yield per tonne of hemicellulose to be higher than a conventional mineral acid-catalyzed process; and being "acid free," the residue is sutable for animal feed.

The core of the technology is a novel, multistep process for extracting the hemicellulose from the corn bran and dehydrating the xylose and arabanose to produce furfural. The products of this process are an aqueous solution containing furfural and a wet corn bran residue. We use toluene to extract the furfural from the the aqueous solution and distill the furfural from the solvent. If the process is integrated with a corn ethanol plant, the wet residue can be combined with the distillers grain and dried. In a stand-alone plant, additional equipment is needed to dry the residue.

We deveoped a fully integrated process design witha heat exchanger network that maximizes waste heat recovery. Process wastewater is treated to removed disolved organic compounds and excess minerals before it is recycled to the process. The only net consumer of water in the process is the cooling towers. Methane generated in the anaerobic wastewater treatment process supplies about 25% of the fuel consumed by the process. The wastewater discharged to the environment is lmited to excess water generated by the dehydration reaction (Eq. 2) and blowdown from the boiler and cooling towers. The process generates no significant amounts of solid waste. Table 3 is a summary of the material and energy balances for the process for a fully heat-integrated process.

5. Technoeconomic Analysis

5.1. Cost Estimates and Profitability

We performed an economic analysis of the proposed furfural process using the recommendations of Kubic et al.²⁷ These recommendations were benchmarked against data for commercial cellulosic ethanol

Table 3. Summary of overall material and energy balances

| Quantity | SI Units | English Units |
|-------------------------|------------------------------|---------------|
| Feeds | | |
| Corn Bran | 8540 kg/hr | 9.41 ton/hr |
| Wash Water | $9.65 \text{ m}^3/\text{hr}$ | 2550 gal/hr |
| Steam (1.7 MPa/250 psi) | 35,200 kg/hr | 77,500 lb/hr |
| Toluene Makeup | 12 kg/hr | 3.8 gal/hr |
| Caustic Soda (50 wt. %) | 57 kg/hr | 125 lb/hr |
| Products | | |
| Furfural | 1720 kg/hr | 3800 lb/hr |
| Wet Corn Bran Residue | 7920 kg/hr | 17,500 lb/hr |
| Utilities | | |
| Natural Gas | 78 GJ/hr | 72 Mscf/hr |
| Cooling Water Makeup | $21 \text{ m}^3/\text{hr}$ | 5600 gal/hr |
| Electricity | 1260 kW | 1260 kW |
| Waste | • | |
| Wastewater Discharge | $3.6 \text{ m}^3/\text{hr}$ | 950 gal/hr |
| Solid Waste | None | None |

plants and are considered unbiased. The methods and assumptions used in this evaluation are consistent with the requirements of an AACE International Class 4 estimate. The economic analysis consisted of four parts – capital cost estimation, operating cost estimation, income estimation, and discount cash flow (DCF) analysis.

We used a factor method to estimate capital costs. We estimated the installed equipment costs inside battery limits (ISBL) and outside the battery limits (OSBL) using Woods' method and cost correlations. 28 The reported uncertainty in the direct costs is $\pm 30\%$. We have assumed that the furfural process is co-located and integrated with a corn ethanol plant, and these expense categories include supervisory and administrative functions that are shared by both plants. Table 4 is a summary of the capital cost estimate.

Table 5 contains the 2018 prices for raw materials, catalysts, and utilities. We determined the internal transfer price of corn bran from its value as a cattle feed based on its protein and carbohydrate content.²⁹ The internal transfer price is price credited to the balance sheet of the co-located ethanol plant for the corn bran used by the furfural plant. We estimated its delivered value to be \$54 per tonne. Based on our survey of rail shipping costs for corn and wheat, the minimum bulk shipping cost for corn bran is about \$27 per tonne. Therefore, we concluded that \$27 per tonne is a reasonable transfer

Table 4. Summary of capital cost estimates used for the furfural process. Estimates are in 2018 US dollars.

| Capital Expense | Nominal Value (million \$) | Standard Deviation (million \$) |
|----------------------------------|-------------------------------|---------------------------------|
| 1. Direct Costs | | |
| A. ISBL Costs | \$17.20 | - |
| B. OSBL Costs | \$8.21 | - |
| C. Other | \$1.50 | - |
| Total Direct Costs | \$26.92 | \$4.65 |
| 2. Indirect Costs | | _ |
| A. Home Office Expenses | \$3.44 | \$1.36 |
| B. Contractor Fees | \$1.52 | \$0.09 |
| C. Contingency | \$9.11 | \$1.17 |
| Total Indirect Costs | \$14.07 | \$1.79 |
| 3. Fixed Capital Investment | \$40.98 | \$4.98 |
| 4. Other Capital Requirements | | |
| A. Land | \$0.82 | \$0.12 |
| B. Spare Parts | \$0.82 | \$0.06 |
| C. Legal Fees | \$0.41 | - |
| D. Working Capital | \$1.27 | \$0.24 |
| E. Startup Expenses | \$6.15 | \$2.38 |
| Total Other Capital Requirements | \$9.47 | \$2.40 |
| 5. Total Capital Investment | \$50.45 | \$6.39 |

Table 5. Raw material, utility, and product prices for 2018. Prices are in 2018 US dollars.

| Material or Utility | Range | Nominal |
|----------------------------------|-----------------------|--------------|
| Raw Materials | | |
| Corn Bran | 0 - 54/tonne | \$27/tonne |
| Toluene | - | \$777/tonne |
| 50 wt. % Sodium Hydroxide | - | \$640/tonne |
| Cooling Water Treatment Chemical | - | \$425/tonne |
| Nutrients for Wastewater | - | \$1005/tonne |
| Treatment | | |
| Utilities | | |
| Natural Gas | \$2.00 - \$10.00/Mscf | \$4.17/Mscf |
| Electricity | \$49.70 - 146.90/MWh | 69.30/MWh |
| Water | - | \$2.01/Mgal |
| Products | | |
| Furfural | \$900 - \$1500/tonne | \$1200/tonne |
| Corn Bran Residue | \$27 - \$184/tonne | \$160/tonne |

price for corn bran in the absence of a local market. Because local market may exist, we consider \$54 per tonne to be an upper bound on price.

Price of natural gas and electricity are 2018 national averages for industrial customers. The upper and lower bounds on prices regional variations in price as well as fluctuations in price during the period from 2008 through 2018. Water costs are based national average municipal water rates for large industrial users. Cooling tower chemicals and consumption rates are based on data from the Strategy Computing Complex at Los Alamos National Laboratory. The prices of other feeds are based on chemical commodity data from 2018. We did not consider uncertainty or variability in the prices of cooling water chemicals and other feeds to the process because they account for about 20% of feed and utility costs, so they only have a minor impact on overall uncertainty.

We estimated operating labor requirements from the process flow diagram using Browns' method, Error! Bookmark not defined. and we assumed that the plant employs five full crews. According to Bureau of labor statistics data, the national average wage for a chemical plant operator in 2018 was about \$30 per hour, and the variability was geographical location was between \$23 per hour and \$35 per hour.

Table 6 is a summary of the annual operating costs and standard deviations for each expense.

The key components of income are product prices and yield. Table 5 contains the nominal product prices and possible ranges for these prices. China dominates the current furfural market; and according to oil consumers, price quotes for Chinese furfural are unreliable. Listed prices for bulk quantities of furfural vary between \$900 and \$2300 per tonne with the majority of prices being in the rate of \$900 - \$1500 per tonne. The price range corresponds to the variability in world prices between 2005 and 2016, so it represents a reasonable range of values. We assumed a nominal furfural price of \$1200 per tonne for this study based on discussions with industrial consumers.

The corn bran residual price is difficult to establish because it is not a material or feed that is currently on the market. Because the residual will be incorporated into the DDGS, we assumed the nominal price to be that average price of DDGS. We expect the residual to be more valuable than the corn bran because the protein content is higher, so the absolute minimum price should be the nominal price of corn bran. We assumed that the upper bound on the corn bran residual to be the upper bound price for DDGS.

Table 7. is a summary of annual income for the process and the standard deviations. The standard deviation for furfural sales includes uncertainty in yield.

The final element of the economic analysis is the DCF analysis. Table 8 gives the parameters that we used for the analysis. We performed the DCF analysis on a real basis, so interest rates and

Table 6. Summary of operating cost estimates used for the furfural process. Estimates are in 2018 US dollars.

| Operating Expense | Nominal Value (million \$/yr) | Standard Deviation (million \$/yr) |
|-------------------------------------|----------------------------------|--|
| 1. Direct Production Costs (Variabl | e) | |
| B. Raw Materials | | |
| Corn Bran | \$1.82 | \$0.69 |
| Toluene | \$0.06 | - |
| 50 wt. % Sodium Hydroxide | \$0.28 | - |
| Cooling Water Chemicals | \$0.04 | - |
| Nutrients | \$0.67 | - |
| Raw Material Subtotal | \$2.87 | \$0.69 |
| C. Utilities | | |
| Natural Gas | \$2.37 | \$0.82 |
| Electricity | \$0.69 | \$0.27 |
| Water | \$0.13 | - |
| Utility Subtotal | \$3.19 | \$0.84 |
| Subtotal | \$6.07 | \$1.08 |
| 2. Direct Production Costs (Fixed) | | |
| A. Operating Labor | \$1.41 | \$0.36 |
| B. Payroll Overhead | \$0.71 | \$0.06 |
| C. Supervision | \$0.14 | \$0.04 |
| D. Laboratory Changes | \$0.14 | \$0.02 |
| E. Maintenance | \$0.98 | \$0.34 |
| F. Operating Supplies | \$0.41 | - |
| G. Royalties and Patents | \$0.41 | \$0.16 |
| Subtotal | \$4.20 | \$0.53 |
| 3. Fixed Charges | | |
| A. Property Taxes | \$0.40 | \$0.12 |
| B. Insurance | \$0.29 | \$0.05 |
| C. Plant Overhead | \$0.28 | \$0.08 |
| Subtotal | \$0.97 | \$0.15 |
| 4. Manufacturing Costs | \$11.24 | \$1.21 |
| 5. General Expenses | | |
| A. Administrative Costs | \$0.41 | \$0.30 |
| B. Distribution and Sales | \$0.52 | \$0.16 |
| C. R&D | \$0.10 | \$0.09 |
| Subtotal | \$1.03 | \$0.35 |
| 6. Operating Costs | \$12.27 | \$1.26 |

internal rate of return are the nominal values minus inflation. The target IRR is based on historical performance of corn ethanol plants, which have an average 20- to 30-year real IRR after taxes of 8% with a range a range of values between 5 and 14%. Therefore, a real IRR of 10% is a realistic, but slightly conservative, target.

The real internal rate of return (IRR) after taxes for the estimated cash flow is 15.7%, which exceeds the 10% target value. Real IRR is the IRR above the prevailing inflation rate. Figure 3 shows the breakdown in production costs. Direct production cost account for nearly half of the total production costs (49%). No single expense dominates the direct productions. The largest expenses are natural gas and labor and supervision. The largest single contribution is capital costs which accounts for one-third of the total cost.

Table 7. Summary of income for the furfural process. Estimates are in 2018 US dollars.

| Income | Nominal Value (million \$/year) | Standard Deviation (million \$/year) |
|-------------------|------------------------------------|--|
| Furfural | \$15.86 | \$1.68 |
| Corn Bran Residue | \$5.43 | \$0.89 |
| Fixed Income | \$21.28 | \$1.90 |

Table 8. Parameters for DCF analysis.²⁷

| _ | | |
|--|---------------------------|----------|
| Parameter | Range | Nominal |
| 1. Technical Factors | | |
| A. Construction time | -25% - +50% of Eq. (3) | Eq. (3) |
| B. Startup Time | 1-6 months | 3 months |
| C. First-year capacity | 60 – 100% design capacity | 80% |
| D. Availability | 60 - 96% | 90% |
| 2. Financial Factors | | |
| A. Plant Life | | |
| Time Horizon | 20 – 30 years | 30 years |
| Salvage Value | 0 - 10% | 0% |
| B. Financing | | |
| Equity financing | 35 - 100% | 60% |
| Interest Rate | 4 - 12% | 5.5% |
| 3. Term of loan | 1-10 years | 7 years |
| C. Corporate Profit Taxes | | |
| Depreciation | Not Applicable | MACRS |
| Depreciation time | Not Applicable | 7 years |
| Federal tax rate | Not Applicable | 21% |
| 4. State tax rate | 0-12% | 6.5% |

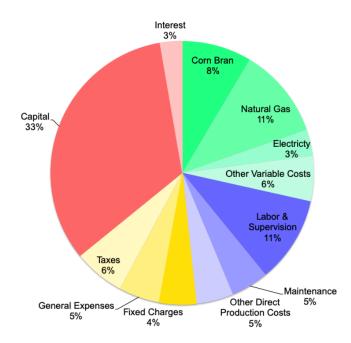


Fig. 3. Production cost breakdown for proposed furfural process. Green = variable direct production costs, purple = fixed direct production costs, gold = fixed charges, general expenses and taxes, red = financial costs.

6.2. Sensitivity and Uncertainty

We performed sensitivity studies and uncertainty analysis on to evaluate the impact of parameter uncertainty, market uncertainty, and lack of knowledge on our results.

We performed a series of sensitivity studies by evaluating the IRR of each parameter at its extreme values. Figure 4 is a tornado plot summarizing the results of the sensitivity analysis for 14 parameters accounting for 95% of the variance in IRR. Extreme values of three parameters – furfural price, corn bran residual price, and natural gas price – reduce the estimated IRR to values below the 10% target value. The sensitivity to corn bran residual price is a greater concern than sensitivity to furfural and natural gas prices. The range of values for furfural and natural gas prices reflect temporary market fluctuations. However, uncertainty in corn bran residual prices is the result of

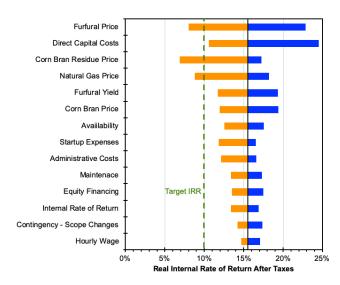


Fig. 4. Sensitivity of real internal rate of return after taxes to parameter uncertainty for the proposed furfural process.

uncertainty in the product value, so deviations from the nominal value are not temporary variations in price.

We performed a statistical analysis of uncertainty to determine the combined impact of uncertainty in all parameters. Figure 14 is a histogram of the Monte Carlo analysis results. The skew of distribution is -0.068 indicting that it is nearly symmetrical. The mean and standard deviation are 10.5% and 5.5%, respectively. Because of skewness in many of the input parameter distributions, the mean value of the IRR is less than the nominal value, but still above the 10% target value. The probability that the IRR is greater than the target value is 0.54. Although the probability of exceed the target IRR is on slightly greater than 50:50, the probability of a negative IRR is 0.027 indicating a low risk of a loss.

6.3. Comparisons with Other Processes

We estimated costs for conventional, sulfuric acid-catalyzed furfural processes with four different feeds – corn bran, corncobs, sugar cane bagasse, and corn stover. The analysis is based on a US location and 2018 prices. We based capital cost estimates, material balance data, and utility requirements for the conventual process on

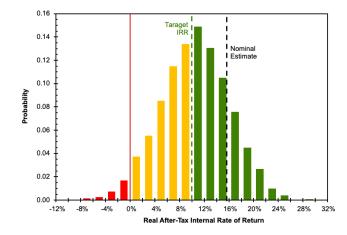


Fig. 5. Histogram for uncertainty in IRR for the furfural proposed process.

Table 9. Comparison feedstocks and processes for furfural production. Based on 13,200 tonne / yr capacity and 2018 dollars.

| Process Type | This Study | Conventional | Conventional | Conventional | Conventional |
|--|-------------|--------------|--------------|--------------|--------------|
| Biomass Data | | | | | |
| Biomass | Corn Bran | Corn Bran | Corncobs | Bagasse | Corn Stover |
| Hemicellulose Content (wt. %) | 44% | 44% | 35% | 25% | 20% |
| Biomass Price (\$/wet tonne) | \$27 | \$27 | \$70 | \$20 | \$75 |
| Biomass Price (\$/tonne hemicellulose) | \$61 | \$61 | \$200 | \$80 | \$374 |
| Capital Investment Summary | | | | | |
| FCI (million \$) | \$41.0 | \$35.5 | \$40.4 | \$47.9 | \$51.9 |
| TCI (million \$) | \$50.4 | \$45.8 | \$53.8 | \$61.9 | \$70.3 |
| Material and Energy Balance Summary | | | | | |
| Biomass Feed Rate (kg/hr) | 8,540 | 11,100 | 14,000 | 19,600 | 24,400 |
| Sulfuric Acid Feed Rate (kg/hr) | - | 64 | 81 | 110 | 140 |
| Caustic Soda Feed Rate (kg/hr) | 55 | 300 | 370 | 520 | 660 |
| Fuel Consumption (MW) | 22 | 24 | 29 | 126 | 152 |
| Biomass Residue Production (kg/hr) | 4,300 | 4,300 | 6,984 | 11,732 | 15,888 |
| Solid Waste Generated (kg/hr) | None | 637 | 972 | 620 | 1,374 |
| Operating Cost Summary | | | | | |
| Biomass (million \$/ tonne) | \$134 | \$174 | \$567 | \$227 | \$1,063 |
| Sulfuric Acid (million \$/tonne) | | \$4 | \$5 | \$7 | \$8 |
| Caustic Soda (million \$/tonne) | \$21 | \$110 | \$139 | \$194 | \$243 |
| Natural Gas (million \$/tonne) | \$174 | \$192 | \$229 | \$301 | \$365 |
| Electricity (million \$/tonne) | \$51 | \$65 | \$81 | \$114 | \$142 |
| Other Operating Costs (million \$/tonne) | \$532 | \$467 | \$674 | \$560 | \$715 |
| Total Operating Cost (\$/tonne) | \$911 | \$1,012 | \$1,695 | \$1,403 | \$2,537 |
| Value of Biomass Residue | Cattle Feed | Fuel | Fuel | Fuel | Fuel |
| Minimum Furfural Selling Prices (\$/tonne) | \$970 | \$1,450 | \$2,270 | \$2,000 | \$3,250 |

DeJong and Marcotullio's analysis of the Multi-Turbo-Column process. ³⁰ Table 9 summarizes the material and energy balances, capital and operating costs, and the DCF analysis results.

The total operating cost for a conventional process with uses corncobs, bagasse, or corn stover are greater than the market value of the products. Therefore, they generate a negative cash flow and have an undefined IRR. Therefore, we used minimum selling price as a metric for comparison, which we computed assuming a 10% real IRR after taxes

For a conventional process, the two factors that have the greatest impact on minimum selling prices are hemicellulose content and the biomass price per tonne of hemicellulose. Biomass with low hemicellulose content requires larger handling and preprocessing

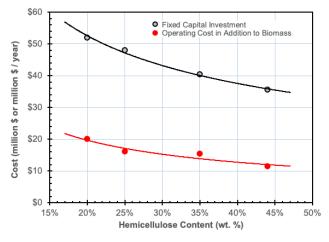


Fig. 6. FCI and annual operating costs of a sulfuric acid catalyzed furfural process as function of hemicellulose content.

equipment than biomass with high hemicellulose content. Low hemicellulose containing biomass also requires more water, more chemicals, and more energy. Thus, fixed capital investment and operating costs other than biomass cost decrease with increasing hemicellulose content, as illustrated in Fig. 6.

As shown in Table 9, the corn bran and bagasse per tonne of hemicellulose are significantly less than the cost of corncobs and corn stover. Both corn bran and bagasse are byproducts of existing processes and are readily available for furfural production. Based on current US farm practices, gathering corncobs and corn stover requires either modifications to existing harvesting methods or additional collection of the harvest residue from the fields. These additional collection costs make corncobs and corn stover expensive sources of hemicellulose.

The combination of high hemicellulose content and low cost makes corn bran a good choice for furfural production. With conventional technology, the minimum selling price for furfural produced from corncobs, bagasse, and corn stover is not competitive with world market prices. A conventional process that uses corn bran as the feed is nearly competitive. The minimum selling prices is near the upper end of the current price range. However, such a process would yield only a 1.7% IRR at the current average price; and therefore, it is probably not competitive.

The proposed process was developed to take full advantage of corn bran as a feed. Because the process does not use mineral acids, the solid residue can be sold as cattle feed generating additional revenue. The increased revenue in combination with a 30% increase in furfural yield and a reduction of chemical consumption enables the proposed process to produce furfural at a minimum. Selling price near the low end of the current price range.

7. Conclusions

Currently, domestic production of furfural from conventional feedstocks using conventional mineral-acid catalyzed processes is not

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competitive on the world market. A major cost driver is the hemicellulose content of the feedstock. The hemicellulose content corncobs, sugar cane bagasse, and corn stover are too low to be competitive. Corn bran is rich in hemicellulose and, therefore, a more economical source of furfural. Because it is a byproduct of corn ethanol production, corn bran-based furfural production can be integrated with an ethanol plant for additional cost savings. Unlike other sources of furfural, the remnants of corn bran can be used as animal feed if free of harmful mineral acid residue. The biomass remnants have a higher protein content than the original corn bran, so it would command a higher price than unprocessed corn bran and increase the profitability of the process

To maximize the economic advantages of corn bran, we have proposed a new furfural process that does not use mineral acids. The expect the that the proposed process will have a higher yield than a conventional process. Also, this new "acid-free" process improves overall economics by increasing the value of the biomass residue and reducing chemical consumption. Use of this proposed process with corn bran as the feed could make US-produced furfural competitive on

the world market. The real rate of return for the process with a furfural price of \$1200 per tonne is 15.7%. Coupling this process with existing corn ethanol plants could improve the profitability of the domestic ethanol industry and provide a competitive domestic source of furfural.

Corn bran or corn fiber combined with the proposed mineral-acidfree process several key advantages for furfural production.

- The furfural yield from the proposed process is expected to be greater than a conventional process, which reduces biomass cost.
- The proposed process is easily integrated with the existing corn ethanol industry ensuring an inexpensive, hemicellulose-rich feedstock for furfural production.
- The high hemicellulose content of corn significantly costs of a furfural process by reducing solids handling.
- The proposed mineral-acid-free process reduces chemical consumption and produces a residue suitable for cattle feed.
- The proposed process generates no solid waste. Therefore, it has a lower environmental impact than current technology.

References

- H. E. Holydoncxx, W. M. van Rhijn, W. van Rhin, D. E. de Vos, and P. A. Jacobs, "Furfural and Derivatives," in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 16, pp. 285 – 313, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany (2012).
- "Furfural Market for Solvents, Pharmaceuticals, Furfuryl Alcohol, and Other Applications: Forecasts, 2016 – 2022," A to Z Research, http://atozresearch.com/chemical-materials/furfural-market-share-growth-by-2022/ (Accessed January 13, 2020).
- 3. R. Kottke, "Furan Derivatives," In *Kirk-Othmer Encyclopedia of Chemical Technology*, (Ed.). doi: <u>10.1002/0471238961</u>.0621180111152020.a01(2000).
- 4. P. Arnold, "Solvent Extraction System," US Patent 2,379,332 (June 26, 1945).
- T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, and A. Manheim, *Top Value-Added Chemicals from Biomass. Vol.* 1-Results of Screening for Potential Candidates from Sugars and Synthesis Gas., US Department of Energy Report No. DOE/GO-102004-1992 (2004).
- A. K. Mathew, A. Abraham, K. K. Mallapureddy, and R. K. Sukumaran, "Lignocellulosic Biorefinery Wastes, or Resources?"
 Chapter 9 in Waste Biorefinery, T. Bhaskar, A. Pandey, S. V. Mohan, D-J Lee, and S. K. Khanal, Eds., pp. 267 297, Elsevier (2018).
- D. T. Win, "Furfural Gold from Garbage," Australian Journal of Technology, 8: 185 – 190 (2005).
- M. Biddy, C. Scarlata, abd C. Kinchin, "Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential," National Renewable Energy Laboratory report NREL/TP-5100-65509 (March 2016).
- 9. I. Agirrezabal-Telleria, J. Requies, M. B. Güemez, and P. L. Arias, "Dehydration of D-Xylose to Furfural Using Selective and Hydrothermally Stable Arenesulfonic SBA-15 Catalysts," *Applied Catalysis B: Environmental*, 145: 34 42 (2014).
- 10. K. Zeitisch, "Furfural Processes," Chapter 10 in *The Chemistry* and *Technology of Furfural and its Many By-Products*, Elsevier Science B. V., Amsterdam (2000).
- 11. G. Natta, "Continuous process for the Production of Furfural and Acetic Acid from Vegetative Material," US Patent 2,8 18413 (December 31, 1957).

- K. Kiminki, R. Kulmála, and S. Sipilä, "Acid Hydrolysis of Polysaccharide-Containing Raw Material," US Patent 4,029,515 (June 14, 1977).
- T. Carlson, J. Dickinson, D. Drew, P. Fagan, F. Gallagher, K. Hutchenson, I. Liberis, K. Mersman, and G. Sunshine, "Process for the Production of Furfural Using a Water Immiscible Organic Solvent," US patent priority number US2019284151 (A1) (September 19, 2019).
- 14. N. Kunthakudee, U. Pancharoen, K. Fulajtárová, T. Soták, M. Hronek, and P. Ramakul, "Salt Effect on the Liquid-Liquid Equilibrium of Water-Furfuryl Alcohol-Furfural System at 298.15 K," Korean Journal of Chemical Engineering, 34: 2293 2300 (2017).
- 15. L. Nhien, N. Long, S. Kim, and M. Lee, "Techno-Economic Assessment of Hybrid Extraction and Distillation Processes for Furfural Production from Lignocellulosic Biomass," *Biotechnology for Biofuels*, 10: 81 – 92 (2017).
- M. Yadav, R. Moreau, and K, Hicks, "Phenolic Acids, Lipids, and Proteins Associated with Purified Corn Fiber Arabinoxylans," *Journal of Agricultural and Food Chemistry*, 55: 943 – 947 (2007).
- 17. H. Noureddine and J. Byun, "Dilute-Acid Pretreatment of Distillers' Grain and Corn Fiber," *Bioresource Technology*, 101: 1060 1067 (2010).
- N. E. Anderson and F. M. Clydesdale, "Dietary Fiber Content of Corn Bran," *Journal of Food Production*, 43: 760 – 762 (1980).
- 19. Z. Hromádková and A. Enringerová, "Isolation and Characterization of Hemicelluloses of Corn Hulls," *Chemical Papers*, 49" 97 101 (1995).
- L. Saulnier, C. Marot, E. Chanliaud, and J-F Thibault, "Cell Wall Polysaccharide Interactions in Maize Bran," *Carbohydrate Polymers*, 26: 279 – 287 (1995).
- 21. A. Enringerová and Z. Hromádková, "Effect of Ultrasound on the Extractability of Corn Bran Hemicelluloses," *Ultrasonic Sonochemistry*, 9: 225 229 (2002).
- D. J. Rose, g. E. Inglett, and S. X. Liu, "Utilisation of Corn (Zea Mays) Bran and Corn Fiber in the Production of Food Components," *Journal of the Science of Food and Agriculture*, 90: 915 924 (2010).
- 23. K. Jiang, L. Li, L. Long, and S. Ding, "Comprehensive Evaluation of Combining Hydrothermal Pretreatment (Autohydrolysis) with Enzymatic Hydrolysis for Efficient Release of Monosaccharides

- and Ferulic Acid from Corn Bran," *Industrial Crops & Products*, 113: 348 357 (2018).
- A. Anukam, B. Goso, O. Okoh, and S. Mamphweli, "Studies on Characterization of Corn Cob for Application in a Gasification Process for energy Production," *Journal of Chemistry*, Article ID 6478389, https://doi.org/10.1155/2017/6478389 (2017).
- 25. M. Pointner, P. Kuttner, T. Obrlik, A. Jäger, and H. Kahr, "Composition of Corncobs as a Substrate for Fermentation of Biofuels," *Agronomy Research*, 12: 391 396 (2014).
- C. P. Mathi, C. A. Löest, F. T. McCollum, and G, R, Hagevoort, Using Byproduct Feedstuff in Grazing Nutrition, New Mexico State University Cooperative Extension Service circular 612 (May 2007).
- W. Kubic, S. Booth, A Sutton, and C. Moore, "Evaluation and Benchmarking of Economic Analysis Methods for Biofuels," Los Alamos National Laboratory report LA-UR-19-30785 (October 2019).
- 28. D. Woods, *Rules of Thumb in Engineering Practice*, Wiley-CVH Verlag GmbH & Co. Weinheim, Germany (2007).
- C. Mathis, C. Löest, F. McCollum, and G. Hagevoort, "Using Byproduct Feedstuff in Grazing Nutrition," Cooperative Extension Service, New Mexico State University, Circular 612 (May 2007).
- 30. W. De Jong and G. Marcotulio, "Overview of Biorefineries Based on Co-Production of Furfural, Existing Concepts and Novel developments," *International Journal of Chemical reactor Engineering*, Vol. 8, Article A69 (2010).

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